

# SCIENCE FOR CERAMIC PRODUCTION

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## CERAMIC MEMBRANES FOR PHOTOCATALYTIC WATER PURIFICATION

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The structure and photocatalytic properties of ceramic membranes synthesized on the basis of amorphous potassium polytitanate intercalated with nickel ions have been investigated. It is shown that the phase composition of the synthesized ceramic depends on the firing temperature: at 650°C it forms from NiTiO<sub>3</sub>, TiO<sub>2</sub> and a residual potassium titanate amorphous phase; at 850°C — NiTiO<sub>3</sub> crystals, mainly present in the surface layer of TiO<sub>2</sub> membranes, and a complex oxide with the composition K(Ti, Ni)O<sub>16.5</sub>, which has a hollandite structure and is present mainly in the structure of the interior layers of the ceramic.

**Key words:** ceramic, composite, structure, photocatalysis.

The overall reduction of the effect of chemical contaminants on humans and the reduction of the effect of humans on the environment to a minimum are two of the most important scientific problems of modern times. The problem of water pollution by hydrocarbons of different classes, contained in sewage from chemical and petrochemical works, is especially acute. A number of methods exist for effective purification of water contaminated with hydrocarbons, but each one has its own substantial drawbacks. For example, anaerobic bacteria cannot be used to purify sewage containing highly toxic components and concentrated salt solutions [1]. The use of adsorption and coagulation creates problems of regeneration of the sorbents and reclaiming the contaminants extracted from water. In recent years a great deal of attention has been devoted to developing methods of photocatalytic purification of water contaminated with hydrocarbons using as the catalyst titanium oxide and its derivatives [2 – 4]. However, the use of modified powders of titanium oxide or titanates in the form of nanoparticles dispersed in the medium to be purified increases the cost of the catalyst considerably and creates the problem of subsequently removing it from the purified water. It has been suggested that the particles of the photocatalyst, which contain alloying additives of precious metals and oxides of rare-earth or transition metals, be deposited on flat substrates which are convenient for exposure to light [5]. But in this case any increase of the efficiency of the photocatalytic decay of hydrocarbons as a re-

sult of the absorption of sunlight in the visible range of the spectrum is negated by the negative effect of a decrease of the area of the solution – catalyst interphase surface [1].

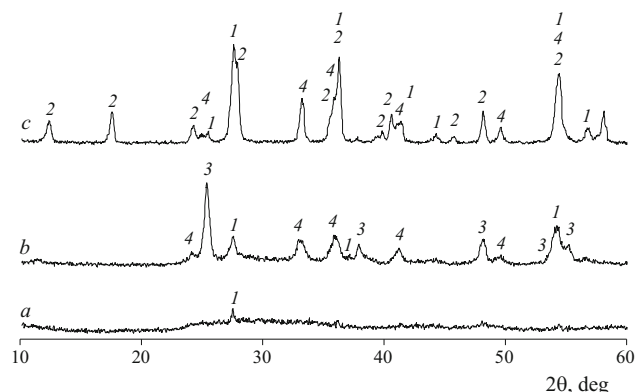
The purpose of the present investigation is to develop a new type of ceramic photocatalyst which gives a high rate of decay of hydrocarbons in aqueous solutions when it is used the form of ceramic membranes based on potassium polytitanate intercalated with transition-metal ions. Nickel was used as the active additive for potassium polytitanate, keeping in mind that with heat treatment of intercalate it can be expected that a ceramic containing semiconductor heterojunctions of the type NiO/TiO<sub>2</sub>, which possess elevated photocatalytic activity in the visible range of the solar spectrum, will be obtained [6]. Potassium polytitanate is chosen as the base material because its nanoparticles, which have a layered structure, are characterized by a high capability for intercalation [7].

Potassium polytitanate (KPT) synthesized following the procedure of [8] during working of titanium oxide powder (rutile, average particle size 7 μm) in melt containing KOH and KNO<sub>3</sub> in the ratio 1 : 8 at temperature 500°C was used for the experiments. The product obtained was washed with distilled water and dried in a desiccator at 60°C.

Intercalation of the nickel ions into the KPT structure was performed from an aqueous solution of the corresponding salt to static adsorption equilibrium. In the process 2 g KPT were placed in 50 ml of nickel chloride solution and held for 24 h with mixing in order to establish adsorption equilibrium. The residue obtained was filtered, dried, and used for

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**Fig. 1.** X-ray diffraction patterns of nickel-ion intercalated KPT (a) and ceramic based on KPT after kilning at 650 (b) and 850°C (c): 1) rutile, 2)  $\text{K}(\text{Ti}, \text{Ni})_8\text{O}_{16.5}$ , 3) anatase, 4)  $\text{NiTiO}_3$ .

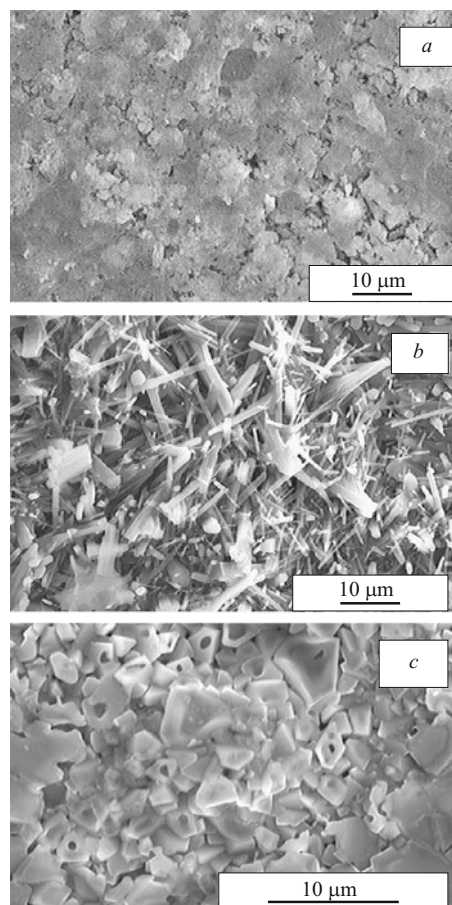
compaction. Blanks of ceramic membranes were made by uniaxial pressing under pressure 260 MPa in a cylindrical steel mold with inner diameter 10 mm; the thickness of the pressed blanks was  $1.0 \pm 0.1$  mm.

The blanks were kilned for 2 h at temperatures 650 and 850°C, chosen on the basis of the results of differential thermal analysis (BAHR STA503 thermal analyzer), which showed the presence of an exothermal peak at 585°C and an endothermal peak at 839°C. The phase composition of the ceramic materials obtained was investigated using a Philips X'Pert MPD diffractometer, while the structure and chemical composition were studied with a Philips XL30ESEM scanning electron microscope equipped with an attachment for local x-ray microanalysis.

The reflection spectrum of the synthesized ceramic membranes in the UV and visible regions of the spectrum were recorded (Evolution-3000 spectrophotometer) to determine the potential photocatalytic activity of the membranes.

The change of the chemical composition of potassium polytitanate before and after intercalation of the nickel ions (in terms of the oxides) is given in Table 1. The results show that the process of intercalation of KPT by nickel ions proceeds by the ion-exchange mechanism and is accompanied by a decrease of the potassium oxide content.

After intercalation the KPT particles retain their x-ray amorphous character (Fig. 1) and are easily pressed, making it possible to obtain a membrane with a high degree of compaction of the particles (Fig. 2). The phase composition of



**Fig. 2.** Frontal electronic photomicrograph of the surface of a ceramic membrane before (a) and after kilning at 650°C (b) and 850°C (c).

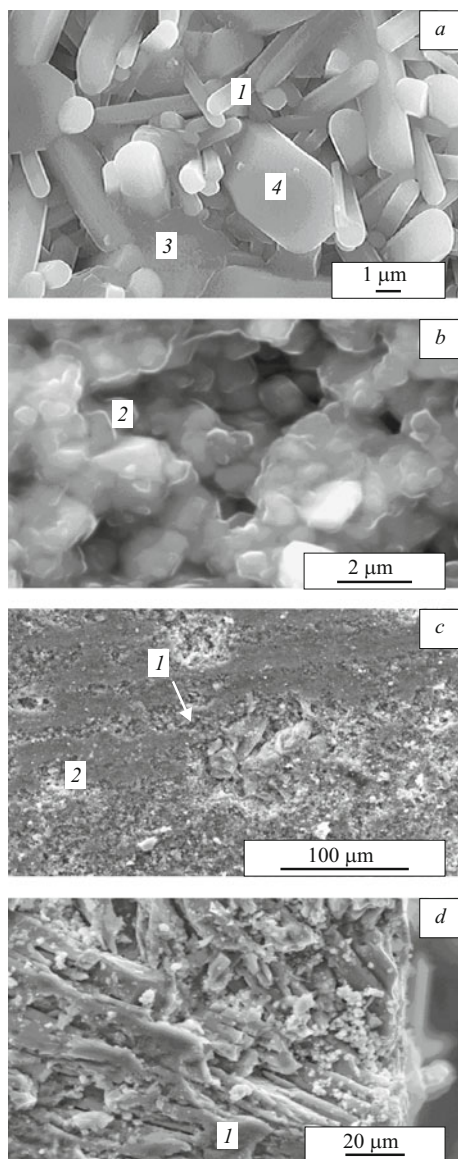
the ceramic obtained after the membranes have been kilned depends on the temperature. According to the data from local x-ray microanalysis, kilning at 650°C results in crystallization of the precursor material with formation of the mixture  $\text{NiTiO}_3$ ,  $\text{TiO}_2$ , and a residual amorphous phase containing mainly  $\text{TiO}_2$  and  $\text{K}_2\text{O}$ .

After the kilning temperature is increased to 850°C the residual amorphous phase melts and interacts with the crystalline phases formed at lower temperatures. As a result, there forms a ceramic composite material consisting of a mixture of  $\text{NiTiO}_3$ ,  $\text{TiO}_2$ , and the complex oxide  $\text{K}(\text{Ti}, \text{Ni})_8\text{O}_{16.5}$ , whose structure is that of hollandite and which is the main phase of the material obtained.

It should be noted that the ceramic material obtained at 650°C possesses a uniform structure in the bulk (Fig. 3) that consists of a ceramic composite in which the residual potassium titanate amorphous phase plays the role of a binder. At the same time the structure of the ceramic membrane synthesized at 850°C is of a distinct gradient character. In the course of kilning, nickel becomes concentrated in the surface layer (Fig. 4). As a result the surface layer of the membrane consists predominately of large  $\text{NiTiO}_3$  crystals, while the in-

**TABLE 1.** Chemical Composition of Potassium Polytitanate Before and After Intercalation by Nickel Atoms (Data from Local H-Ray Microanalysis)

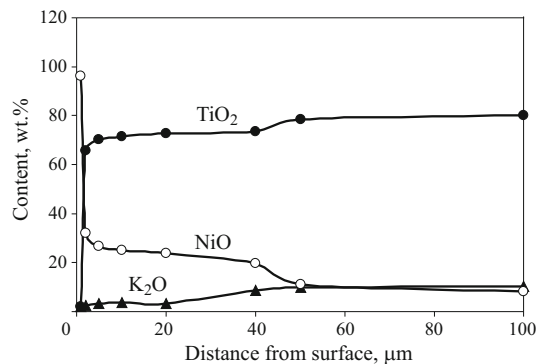
Sample	Oxide content, wt. %		
	$\text{K}_2\text{O}$	$\text{TiO}_2$	NiO
Initial	19.4	80.6	—
Intercalated	8.3	79.2	12.5



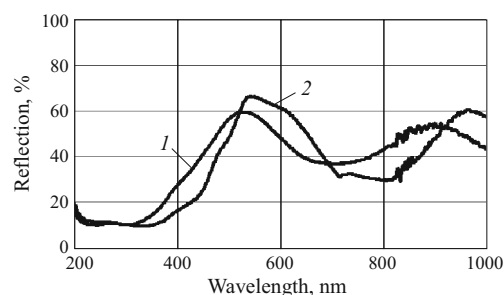
**Fig. 3.** Electron photomicrographs of a transverse section of a ceramic membrane: the structure of the interior layers of the ceramic obtained after kilning at 650°C (a) and 850°C (b); structure of the ceramic obtained after kilning at 850°C; interior zone (c) and near-surface zone (d): 1)  $\text{NiTiO}_3$ ; 2)  $\text{K}(\text{Ti}, \text{Ni})\text{O}_{16.5}$ ; 3) amorphous phase; 4)  $\text{TiO}_2$ .

terior layers of the material are formed mainly from hollandite. Crystals of metallic nickel form on the surface of the membrane.

The surface texture of the material, acceptable for direct action of solar radiation under exposure, is important for using ceramic membranes as photocatalysts. The surface texture of the ceramic membrane obtained after kilning at 650°C looks is more attractive from this point of view, since it has a larger geometric layer represented by fibrous crystals of nickel titanate (see Fig. 2). On the other hand the surface of a membrane obtained at 850°C has numerous inclusions of crystals of metallic nickel. The presence of metallic nickel



**Fig. 4.** Distribution of the elements in the surface layers of ceramic synthesized at 850°C (in terms of oxides).



**Fig. 5.** Optical absorption spectra of ceramic synthesized at different temperatures on the basis nickel-intercalated KPT.

can impart to the surface an additional photocatalytic activity [9]; in addition, the photocatalytic activity of hollandite-like structures with the composition  $\text{K}(\text{Ti}, \text{Ni})_8\text{O}_{16.5}$  has still not been studied.

The optical reflection/absorption spectra of ceramic membranes kilned at different temperatures are presented in Fig. 5. The results obtained show that the ceramic samples are characterized by intense absorption of solar radiation in the visible region of the spectrum, while an increase of the kilning temperature results in a strong shift of the fundamental absorption band into the visible region; moreover, the intensity of radiation absorption increases in the region 550 – 700 nm. All this must give a high photocatalytic activity of the experimental materials in the course of decomposition of hydrocarbons dissolved in water.

The comparative catalytic activity of the membranes was evaluated for the example of the model reaction of decomposition of hydrogen peroxide (formation rate of gaseous products) in an aqueous solution [1 – 5]. Table 2 gives the results obtained with ceramic membranes synthesized on the basis of pure potassium polytitanate and KPT intercalated with Ni ions and kilned at different temperatures. Analysis of the results showed that the ceramic composites synthesized on the basis of potassium polytitanate intercalated with nickel ions possess 2-fold higher photocatalytic activity as compared with potassium tetratitanate, forming the structure

**TABLE 2** Decomposition Rate of Hydrogen Peroxide on the Surface of Different Ceramic Membranes

Membrane	Kilning temperature, °C	Decomposition rate of H <sub>2</sub> O <sub>2</sub> , 10 <sup>-2</sup> ml/(min · cm <sup>-2</sup> )
KPT	—	0.71 ± 0.20
KPT/Ni	650	1.55 ± 0.25
	850	1.43 ± 0.22

of a ceramic based on pure potassium polytitanate and absorbing solar radiation only in the UV region of the spectrum [1]. It is also important to note that even though radiation absorption is weaker in the visible region of the spectrum, the ceramic membrane synthesized at 650°C is somewhat more active photocatalytically. This fact can be explained by the more extended surface of such membranes, which is formed by fibrous crystals of nickel titanate.

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